Chapter 1

Introduction and Literature Review

1.1 The atmosphere

Language and formality!!

The atmosphere is made up of various gases held to the earths surface by gravity. These gases undergo transport on all scales, from barbeque smoke being blown into your face to smoke plumes from forest fires travelling accross the world and depositing in the antarctic snow. They take part in various chemical reactions along the way, largely driven by solar input and interactions with eachother. Various chemicals are lofted into the atmosphere by soil, trees, factories, cars, seas and oceans, you name it. They are also deposited back to the surface both directly and in rain drops.

Mostly the atmosphere is made up of nitrogen (N_2: $\sim$ 78%), oxygen (O_2: $\sim$ 21%), and argon (Ar: $\sim$ 1%). Water (H_2O) ranges from 0.001 to 1% depending on evaporation and precipitation. Beyond these major constituents the atmosphere has a vast number of *trace gases*, including carbon dioxide (CO_2: $\sim$ 0.4%), Ozone (O_3: .000001 to 0.001%), and methane (CH_4: $\sim$ 0.4%) Brasseur and Jacob, 2017, Ch. 2. Trace gases in the atmosphere can have a large impact on living conditions. They react in complex ways with other elements (anthropogenic and natural), affecting various ecosystems upon which life depends.

don't capitalise chemical species

Most of the atmosphere ($\sim$ 85%) is within 10 km of the earths surface. This is due to air pressure, which decreases logarithmically with altitude. Imagine you are lying at the bottom of the ocean, except that ocean is made up of air. The pressure we are subjected to is from the weight of all the air above us.

1.1.1 Structure

The atmosphere extends above us to the edges of space. This is split into various layers, defined by the *lapse rate*: the decrease in temperature as we ascend. Figure 1.1 shows the pressure and temperature profiles as we head upwards through the atmosphere. First we have the troposphere, which extends to roughly 10 km and is characterised by increasing positive lapse rate (or decreasing temperature with altitude). At the top of the troposphere (the tropopause) the temperature stops decreasing, and then the stratosphere is defined by a negative lapse rate. This is due to UV light being absorbed by ozone, and leads to a very vertically stable environment.

radiation

define properly e.g. $-dT/dz$

is it increasing? or just positive?

In addition to these atmospheric layers, it is helpful to split the troposphere further: into a *boundary layer*, and the *free troposphere*. The *boundary layer* is the lowest layer and involves increased atmospheric mixing due to ground heating and friction effects. It generally extends anywhere from 200 - 1000 m, above which the ground affects have

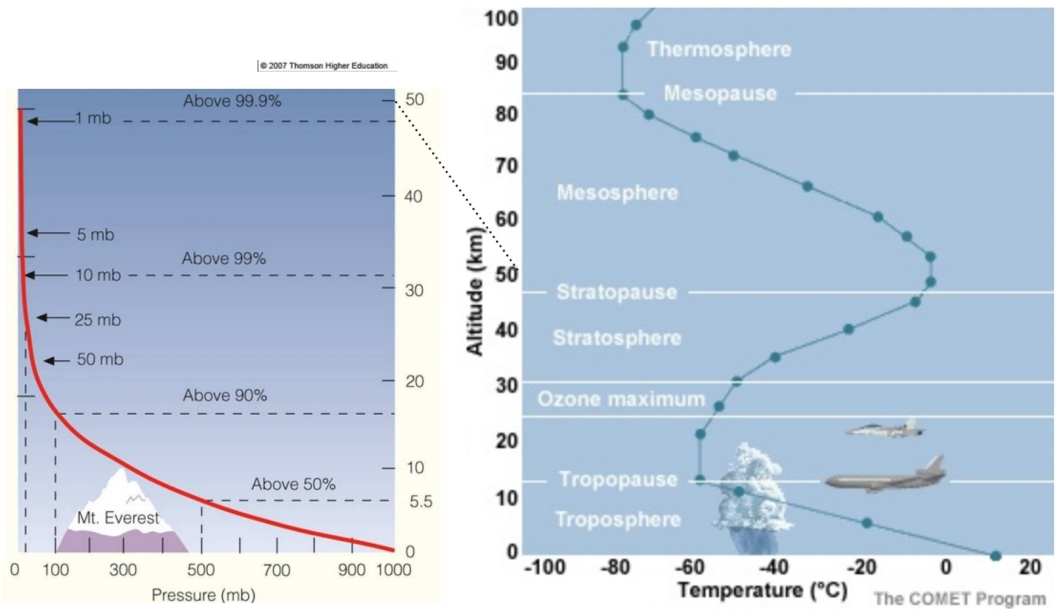

FIGURE 1.1: Pressure (red) logarithmically decreasing, shown with percentage of atmosphere below at several points. Temperature (green) changes throughout the atmosphere. Figure edited from https://climate.ncsu.edu/edu/Structure.

"less impact" or "fewer direct impacts"

less direct impacts. The *free troposphere* is the remainder of the troposphere and is more affected by transport, both horizontally and from the stratosphere.

1.1.2 Chemistry - perhaps "Composition" more appropriate?

This is jarring - need some sort of overview to transition here

Hydroxyl radicals

The OH radical drives many processes in the atmosphere, especially during the day when photolysis of ozone drives OH concentrations (Atkinson, 2000). OH is a key species which reacts with nearly all the organic compounds in the troposphere. The exceptions are chlorofluorocarbons (CFCs), and Halons not containing H atoms (Atkinson, 2000). OH and HO_2 concentrations largely determine the oxidative capacity of the atmosphere. Oxidation and photolysis ~~(splitting by photons)~~ are the two main processes whereby compounds are broken down in the atmosphere. Over land, isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) account for 50% and 30% of the OH reactivity respectively (Fuentes et al., 2000).

relevance?

→ key point, start with this

what is this? define/explain (but probably not in this section!)

Before yyyy, ~~In the late 90's~~ it was thought that OH radicals were ~~are~~ formed exclusively from photolysis of O_3, HONO, HCHO, and other carbonyls ($R_2C{=}O$) Atkinson, 2000. Isoprene (C_5H_8) was thought to be a sink of OH until it was shown by Paulot et al., 2009b that the radicals are recycled. This recycling process is discussed in more detail in section 1.3.3.

Something missing - what is thought now?

Ozone is an important precursor to OH, as excited oxygen atoms ($O(^1D)$) are created through its photolysis, which then go on to ~~mix~~ react with water ~~and~~ to form OH, as reaction sequence

shown in this equation ~~taken from~~ [Atkinson, 2000] just cite

50

$$
\begin{aligned}
O_3 + \text{hv} &\rightarrow O_2 + O(^1D) && (\lambda \leq \cancel{335}\text{nm}) \\
O(^1D) + M &\rightarrow O(^3P) + M && (M = N_2, O_2) \\
O(^3P) + O_2 + M &\rightarrow O_3 + M && (M = \text{air}) \quad \text{why different?} \\
O(^1D) + H_2O &\rightarrow 2OH &&
\end{aligned}
\tag{1.1}
$$

that

This shows ~~how~~ some of the $O(^1D)$ recycles back to Ozone, while some forms OH. ~~NB: The wavelength was updated to 350 nm in~~ [Atkinson and Arey, 2003].

comment on relative rates of these, use 1.1a, 1.1b etc. to discuss

jarring! you were making a point about importance of ozone. Why are you suddenly discussing NOx? Fit better in O_3 section?

NOx

vague.. chemical family

NO_X ($\equiv NO_2$ and NO) is another important group in the atmosphere due to the various [reactions it initiates.] Power generation and combustion transport emissions are the main sources of NO_X[.] If NO and O_3 are both [in the atmosphere], the following reactions (Atkinson, 2000) occur:

By definition both are "in the atmosphere"

$$
\begin{aligned}
NO + O_3 &\rightarrow NO_2 + O_2 && \\
NO_2 + O_3 &\rightarrow NO_3 + O_2 && \\
NO_3 + \text{hv} &\rightarrow NO + O_2 && (\sim 10\%) \\
NO_3 + \text{hv} &\rightarrow NO_2 + O(^3P) && (\sim 90\%)
\end{aligned}
\tag{1.2}
$$

???? are you sure? I think you are talking about titration but first level effect is more pollution.

Which generally leads to lower ozone concentrations in cities due to the NO_X pollution.

vague

Since radicals play such a big role in regulating [many chemical reactions] in the atmosphere it's important for models to accurately represent them (eg. **Travis2014**). This is difficult as they are coupled with so many other species and measurements of OH are not readily available on a global scale. – is this paragraph in the right place? doesn't seem relevant

1.2 Ozone

Ozone (O_3) is mostly located in the stratosphere, where it helpfully prevents much of the shorter wave length solar radiation from reaching the earth's surface (ie UV light). In the stratosphere ozone production is generally driven by the Chapman mechanism, as high energy light (with wavelengths $\lambda < 242$ nm) photolyses the molecular oxygen (O_2) in the atmosphere (Brasseur and Jacob, 2017, Chapter 3, section 2).

is there another source?

The Chapman mechanism involves several equations which lead to rough equilibrium of O, O_2, O_3 and pressure, as follows:

different format from above

$$
\begin{aligned}
O_2 + h\nu(\lambda < 242\text{nm}) \rightarrow &\quad O + O \\
O + O_2 + M \rightarrow &\quad O_3 + M \\
O_3 + h\nu(\lambda < 1180\text{nm}) \rightarrow &\quad O + O_2 \\
O + O_3 \rightarrow &\quad O_2 + O_2
\end{aligned}
\tag{1.3}
$$

should have been defined 1st time used.

Where $h\nu$ represents radiation and M is an inert molecule (such as N_2). The high energy photons ($\lambda < 242$ nm) are present from the top of the atmosphere but are mostly removed before reaching the troposphere. The lifetime of O against loss by O_2 is less than a second in the troposphere, and produced O_3 quickly returns to O and O_2, as low energy ($\lambda < 1180$ nm) light and M are abundant. The gradient of light penetration in addition to the logarithmic decrease in atmospheric pressure (which affects M abundance) drives the vertical profile of ozone into what is called the ozone layer, where we have relative abundance of ozone in the stratosphere. This mechanism requires radiation so only takes place during the daytime, during the night there are different processes driving ozone chemistry. in the strat? Makes it sound like O_3 layer disappears at night.

how?

vague. decrease towards surface?

→ in which orientation?

troposphere

Ozone in the lower atmosphere is a serious hazard that causes health problems (Hsieh and Liao, 2013), damages agricultural crops worth billions of dollars (Avnery et al., 2013; Yue et al., 2017), and increases the rate of climate warming (Myhre and Shindell, 2013). Around 5 to 20 percent of all air pollution related deaths are due to ozone (Monks et al., 2015), roughly .8 million deaths per year (Lelieveld et al., 2013). In the short term, ozone concentrations of ~50-60 ppbv over eight hours or ~80 ppbv over one hour are agreed to constitute a human health hazard (Ayers and Simpson, 2006; Lelieveld et al., 2009). Long term exposure causes problems with crop loss and ecosystem damage (Ashmore, Emberson, and Murray Frank, 2003), and worryingly concentrations may get worse in the future (Lelieveld et al., 2009; Stevenson et al., 2013). Further tropospheric ozone enhancements are projected to drive reductions in global crop yields equivalent to losses of up to USD_{2000}$ 35 billion per year by 2030 (Avnery et al., 2013), along with detrimental health outcomes equivalent to ~USD_{2000}$11.8 billion per year by 2050 (Selin et al., 2009). Recently Yue et al., 2017 showed that the net effect of near-surface ozone on is a ~ 14% decrease in net primary productivity (NPP) in China. They state that drastic measures could reduce the decrease by ~ 70% by 2030.

This paragraph would be a good way to motivate @ start of thesis — trop O_3 is what your thesis is about!

Since the Montreal Protocol on Substances that Deplete the Ozone Layer was established in August 1987, and ratified in August 1989, several satellites and many measurement stations were set up to monitor ozone in the stratosphere. However, in the southern hemisphere there are relatively few records of ozone (Huang et al., 2017). This affects our ability to accurately determine sources of ozone in the troposphere.

Models of ozone in the atmosphere are used broadly for international assessments of ozone related emissions (Young et al., 2017). Young et al., 2017 summarise current global ozone modelling standards and the metrics and processes used to evaluate these models. They show how models can be used to improve measurements, estimate concentrations in regions not sampled, and allow analysis of other processes which involve ozone (such as radiation).

Not sure these 2 paragraphs belong here, esp. model one (which doesn't say much right now)

Generally there are two main drivers of tropospheric ozone concentrations: transport from the stratosphere and chemical production due to emissions of precursors. Globally, most tropospheric ozone is produced by naturally emitted (biogenic) precursors. At small to medium scales, pyrogenic (fire) and anthropogenic (man-made) emissions can be important. Smoke plumes from biomass burning can carry ozone precursors, creating higher ozone concentrations downwind of the plume's source. Emissions of precursors from large cities (such as NO_X emissions from traffic and power production) can impact ozone concentrations.

Is that definitely true? Do you have #'s & refs to back this up?

vague.

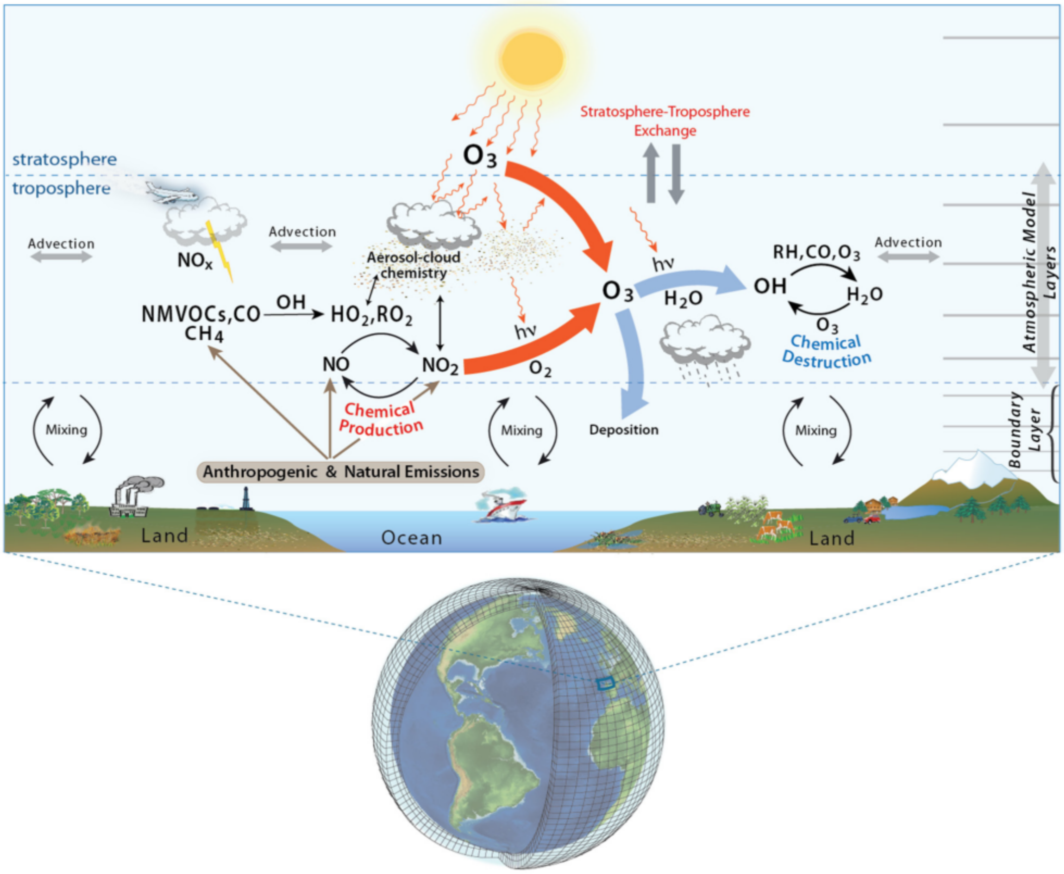

FIGURE 1.2: Tropospheric ozone processes, Figure 1 in Young et al., 2017. DOI: https://doi.org/10.1525/elementa.265.f1

don't frame around models here. Frame in terms of actual processes. Highlight where your work fits in.

A good summary of processes affecting tropospheric ozone, copied from Young et al., 2017, is shown in Figure 1.2. This picture shows the major processes used by global chemistry models when simulating tropospheric ozone. In each gridbox both physical and chemical processes need to be accounted for.

1.2.1 Stratosphere to troposphere transport

Historically (in the late 1990's), ozone transported down from the stratosphere was thought to contribute 10-40 ppb to tropospheric ozone levels, matching tropospheric production (Atkinson, 2000; Stohl et al., 2003). This number was revised down over the years as measurement and modelling campaigns improved our understanding of global scale transport, mixing, and chemistry (Monks et al., 2015). Recently Kuang et al., 2017 analysed various measurements in south-east USA and observed STT influence which can be seen to affect surface ozone levels. In their work they use various measurements from different instruments to give the structure and temporal evolution of ozone and the local weather system.

Ozone transported to the troposphere from the stratosphere can occur through diffusion (relatively slowly), or direct mixing. Intrusions of stratospheric air into the